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Aqueous Immiscible Layered Double Hydroxides: Synthesis, Characterisation and Molecular Dynamics Simulation

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We describe a novel post treatment for layered double hydroxide (LDH) materials using aqueous immiscible (AIM) solvents resulting in improved surface area and powder flow. The effect of solvent functional groups and structure are explored, aided by molecular dynamics simulation of AIM-LDH washing.

In recent years, layered double hydroxides (LDHs) have gained significant attention for use in catalysts and supports,[1-3] adsorbents,[1, 4, 5] flame retardant materials and polymer additives;[6, 7] owing to their highly tuneable composition and morphology.[8-10] Primary LDH particles intercalated with inorganic anions usually yield low surface areas (5−15 $m^2 g^{-1}$).[11] It was reported that LDHs can be delaminated in formamide, butanol, and acrylate to increase surface area.[12-16] Recently, O'Hare and co-workers discovered a novel post-synthesis step[17-19] that dramatically increases LDH dispersion and organophilicity by using aqueous miscible organic solvent treatment, yielding materials known as aqueous miscible organic layered double hydroxides (AMO-LDHs).[17,20] The composition of AMO-LDHs is defined as $[M^{z+}_{1-x}M'^{y+}_{x}(OH)_2]^{a+}(X^{n-})_{a/n}\cdot bH_2O$ *c*(AMO-solvent), which distinguishes them from the general formula of LDHs, $[M^{z+}_{1-x}M'^{y+}_{x}(OH)_2]^{a+}(X^{n-})_{a/n}\cdot bH_2O$, wherein *M* and *M'* are metal cations, $z = 1$ or 2; $y = 3$ or 4, $0 < x < 1$, $b = 0$-10, $c = 0$-10, X is an anion, *n* is 1 to 3 and $a = z(1 - x) + xy - 2$.[19] It has been observed that the AMO-LDHs can be readily dispersed in non-polar hydrocarbon solvents and exhibit significantly higher surface areas.[19, 20] It was postulated that the organic solvent should be fully miscible with water in order to replace the surface bound water from the surface of primary LDH particles for the effect to work. As LDHs are prepared at scale from aqueous precipitation, such a treatment step is facile and scalable. Furthermore, Erastova *et al.*[21] observed that the addition of AMO solvents disrupts LDH interlayer hydrogen bond networks as a function of solvent concentration. At low concentrations, solvents are entirely localised in the bulk water region, behind the second hydration layer (the continuous water film) of the LDH surface. At higher concentrations, AMO solvent distributions additionally feature a small contribution behind the first hydration layer. At the highest concentrations, adsorption of non-cyclic AMO solvents onto the LDH surface was observed. All the AMO solvent species studied feature a specific alignment, indicating a strong interaction with the surface. As a consequence, the AMO solvent's non-polar region orient away from the surface, weakening the H-bond network between the first and second water hydration layers at the mineral interface.

Herein, the use of non-AMO solvents will be examined in the post-production stage of LDH synthesis, and the resulting LDH properties compared with AMO solvent treated ones. This non-AMO solvents treatment is identified as an aqueous immiscible organic solvent treatment (so called AIM). The shorthand term AMO-LDHs and AIM-LDHs are given for AMO and AIM solvents treated LDHs, respectively.

In this study, both AMO and AIM solvents were used: alcohol (ethanol), ester (ethyl acetate), ether (diethyl ether) and two hydrocarbon (hexane, toluene) solvents. These solvents were chosen due to their different functional groups and miscibility with water. After washing the LDHs with deionised (DI) water several times to reach neutral pH, the LDH particles were rinsed and re-dispersed in a certain solvent for four hours. The LDHs were easily dispersed in ethanol (AMO), ethyl acetate and diethyl ether (AIM) but not in toluene and hexane (hydrocarbon).

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In order to further quantify the molecular mechanism behind AIM, we carry out molecular dynamics (MD) simulations of $Mg_6Al_2(OH)_{16}CO_3$-LDHs, treated with the aforementioned organic solvents. To replicate solvent washing we gradually substitute water for solvent in three steps in the simulated systems.

The X-ray diffraction (XRD) patterns, Brunauer-Emmett-Teller (BET) surface areas and densities of AMO- and AIM-LDHs with various washing solvents are shown in Fig. S1-S3. They show similar XRD patterns, indicating that both AMO and AIM treatments do not visibly affect the structure of the LDHs. The *d*-spacing of both (003) and (110) Bragg reflections remain unchanged, suggesting that no detectable intercalation or swelling of the LDH after solvent treatment occurred. Using Scherrers' equation, a large reduction in the stacking domain length of LDHs from about 260 to 30 Å can be determined, making the number of stacked LDH layers decrease from 35 to 4 layers after treatment, indicating the role of solvent in the formation of thinner primary platelets.

The specific surface areas of LDHs (determined by the N_2 BET method) increase dramatically from 9 to almost 380 $m \cdot g^{-1}$ after solvent treatment. All LDHs exhibit type IV isotherm and H3 type hysteresis loop which represents the plate-like particles with slit-shape pores of LDHs (Fig. S4). Pore size distribution curves (determined by the Barrett-Joyner-Halenda (BJH) analysis) show large mesopores; some macropores developed after solvent treatment (Fig. S5). The micropores contribute to the near edge zone of the interlayer region and the meso/macropores are attributed to the external surface area of the LDH platelets.

Fig. S6 shows the TGA and the first derivative curves (DTG) of different solvent-treated LDHs. It can be seen from the mass loss below 250 °C that the diethyl ether treated LDH produces two mass loss peaks of which the first is believed to be due to loss of diethyl ether. Hydrocarbon solvents (such as hexane and toluene) exhibit a broad peak in this region making solvent content determination difficult. Therefore, the amount of solvent in LDHs "(*c*) value" in the LDH formula can be determined by elemental analysis (summarised in Tables S1 and S2). The solvent is probably bound to the surface of the LDH via hydrogen bonding and/or intercalated in the galleries of the LDH. Water content in the conventional LDHs (water washed) is 0.634 (Table S3). In toluene and hexane washed LDHs (with dispersion time of 4 hours), their water contents are 0.402 and 0.548 (Table S2) for toluene and hexane washed LDHs respectively. These are slightly less than water washed LDHs but more than those washed with the other solvents used in this study. Furthermore, their AIM-solvent contents are still very low (0.001 and 0.002 for toluene and hexane washed LDHs respectively).Time dependence studies using toluene and hexane are shown in Fig. S7 and S8.

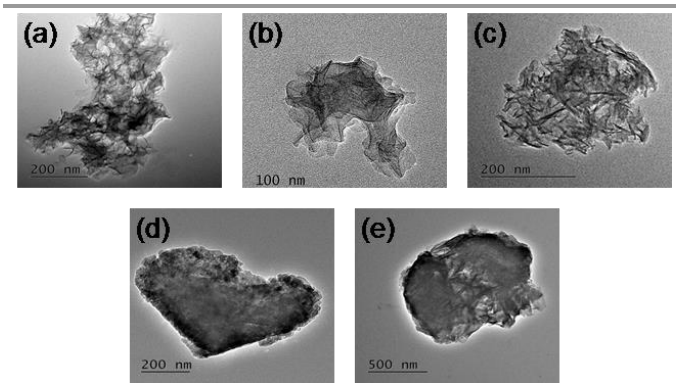

Fig. 1 TEM images of different AMO and AIM solvent-treated Mg_4AlCO_3–LDHs. (a) ethanol, (b) ethyl acetate, (c) diethyl ether, (d) toluene, and (e) hexane.

The change in morphology of AMO and AIM treated LDHs was studied by TEM (Fig. 1). Both AMO- and AIM-LDHs exhibit thin platelets and are less aggregated, which suggests delamination of LDHs after solvent treatment as seen in Chen *et al.*.[19]

To further explore the efficiency of AIM treatment in comparison with AMO treatment, MgAl-CO_3 LDHs with different Mg/Al ratio were synthesised. The number of LDH layers decreases, after solvent treatment, for all Mg/Al ratios. In accordance, the nitrogen BET surface area of LDHs dramatically increases from 8–15 m^2/g to 300-330 m^2/g in diethyl ether and 370-420 m^2/g in ethyl acetate; indicating the formation of thinner platelet LDHs (Fig. 2). The composition of these LDHs is shown in Tables S3.

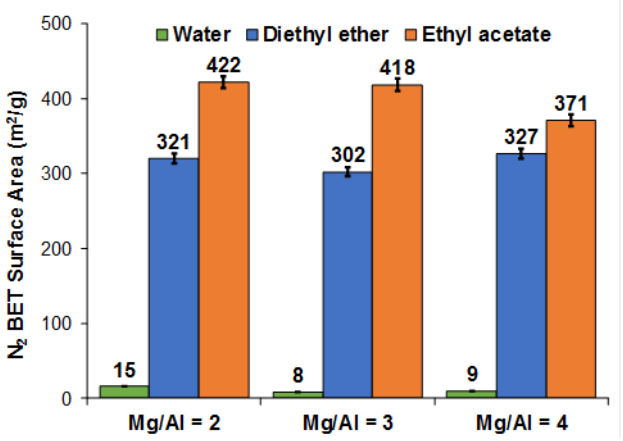

Fig. 2 N_2 surface area of various Mg:Al LDHs ratios washed with water (conventional), and diethyl ether and ethyl acetate (AIM-LDHs).

Molecular dynamics simulations have been carried out for three concentrations of each of the solvent in water at the LDH surface. Their equilibrated conformations are shown in Fig. S9 - S13. For comparison partial densities and H-bonding densities for pure water system are shown in Fig. S14, and for the solvent-water mixtures in Fig. S15. The vectorial alignment of solvent as a distance from the surface is given in Fig. 3. Snapshots of solvent treated systems show that at low concentration; ethanol, ethyl acetate and diethyl ester mix into the bulk of the water, while toluene and hexane form a layer in the bulk (Fig. S9 - S13). As the solvent concentration increases, solvents appear closer to the surface of the LDH. From the density profiles shown in Fig. S15a, we can see that AMO solvent ethanol enters the space behind waters in the first hydration shell, while non-

AMO solvents do not. While examining the H-bond density profile, it can be seen that as the solvent concentration increases, disruption of the H-bond network occurs (Fig. S15b). In the case of the AMO solvent (ethanol), and AIM solvents (ethyl acetate and diethyl ether), the reduction of H-bonding density occurs at the second hydration shell, while in the case of hexane and toluene the H-bond distortion only occurs where the organic solvent layer is formed. The AMO solvent (ethanol) accumulates closer to the surface, and is strongly aligned by it, while the AIM solvents ethyl acetate and diethyl ether accumulate further from the surface but are also strongly aligned by it (Fig. 3).

As already observed by Erastova *et al.*[21], in agreement with this study, the surface affects the arrangement of polarisable solvent molecules (water, AMO and AIM) over 1.5 nm away from the LDH surface itself. This is due to the interplay between Van der Waals and electrostatic forces. Therefore, direct contact between AMO and AIM solvent and LDH surface is not necessary to destabilise interlayer interactions. LDH surfaces align AMO and AIM solvents in such manner that organic groups point away from the surface, producing a hydrophic-like coating that makes LDH layers more dispersible in organic solvents, as observed experimentally by Chen *et al*. [19, 20]

This is not the case for non-polar hexane and toluene which show very slight preferential alignment, mainly due to the formation of the immiscible phase above the water layer. Toluene and hexane are defined as weak hydrogen bonding solvents. At short dispersion time (e.g. 4 hours), structural water of LDH is partially replaced (as shown in the water content). Hence, those LDHs are still aggregated after solvent treatment (as shown in Fig. 1).

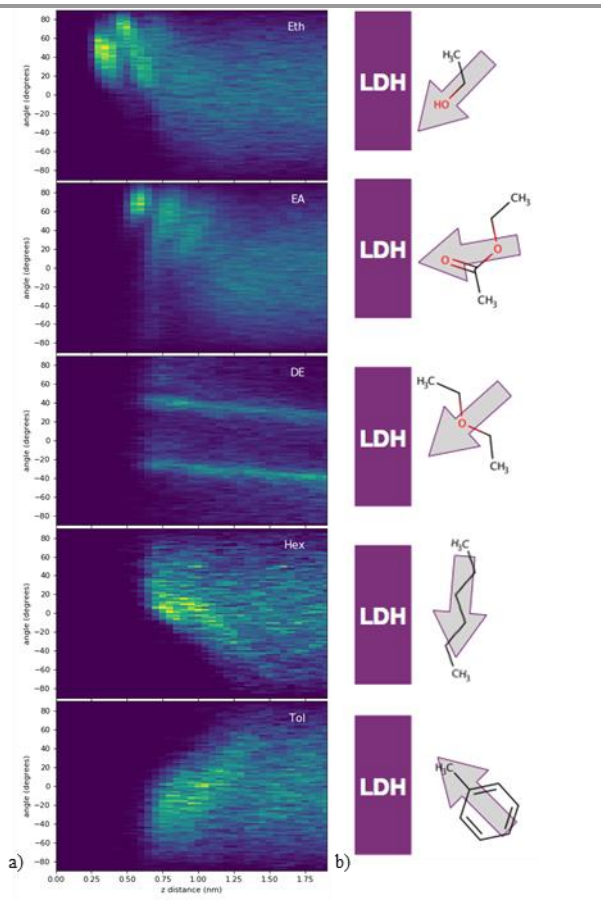

Fig. 3 a) vector assigned to the molecule, as grey arrow, and its preferential alignment to the LDH surface, shown in palatinate and b) angle of solvent molecules with respect to their distance from the LDH surface. Scale from blue to yellow corresponds to the increase of solvent density at a particular angle.

Considering the structure and functional groups of each solvent, a similarity for all of them is hydrogen bonding potential. We have hypothesised that the strength of interaction between water molecules, present between the layers of the LDHs or on its surface, can be efficiently reduced by a polar organic solvent having hydrogen bonding characteristics (hydrogen bond donor or acceptor). This allows some of the residual water to be effectively replaced, disruption of the strong interparticle hydrogen bond networks, and the LDH layers to come apart. The solvent interacts with the LDH layers hydroxyl groups *via* hydrogen bonding and replaces the surface bound water of the LDH, thereby resulting in a fluffy and high surface area LDH product. By considering the definition of conventional hydrogen bonding, all AMO and most AIM can be identified as conventional hydrogen bonding solvents.[22, 23] In 1999, Desiraju and Steiner gave a definition for a new type of hydrogen bonding, so called 'weak hydrogen bonding', as an interaction X–H···A.[24] It is now clearly recognised that X can be any element having higher electronegativity than H, and A could be any elements and also π-electrons.[25, 26] Hence, hydrocarbon and halogenated solvents can be recognised as weak hydrogen bonding solvents.

In summary, a novel post-production organic solvent treatment step for LDHs using an aqueous immiscible organic solvent treatment (AIM solvent) has been investigated. We proposed that the hydrogen bonding characteristics of the solvent play an important role for

removing residual water present between the layers or on the surface of the LDHs. Polarity might also affect the final LDH products obtained. Further studies are currently in progress.

The solvent treatment results in a finer, free-flowing LDH powder with a very high surface areas and low powder density compared to conventional LDHs. This study allows flexibility of solvent selection for future applications. Furthermore, the use of AIM treatment could greatly enhance the efficiency of the manufacturing process, allowing the solvent to be easily separated from the displaced residual water and readily recycled for use leading to enhance properties for packaging (reduction in water vapour transmission rate) and catalysis applications (increase in polymerisation ethylene activity and in processibility due to better, more desirable, morphology).

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Notes and References

"There are no conflicts to declare".

1. C. Li, M. Wei, D. G. Evans and X. Duan, *Small*, 2014, **10**, 4469-4486.
2. F. Cavani, F. Trifirò and A. Vaccari, *Catal. Today*, 1991, **11**, 173-301.
3. S. Omwoma, W. Chen, R. Tsunashima and Y. F. Song, *Coord. Chem. Rev.*, 2014, **258–259**, 58-71.
4. S. P. Newman and W. Jones, *New J. Chem.*, 1998, **22**, 105-115.
5. K. H. Goh, T. T. Lim and Z. Dong, *Water Res.*, 2008, **42**, 1343-1368.
6. S. Guo, D. G. Evans and D. Li, *J. Phys. Chem. Solids*, 2006, **67**, 1002-1006.
7. D. G. Evans and X. Duan, *Chem. Commun.*, 2006, 485-496.
8. X. Duan and D. G. Evans, *Layered Double Hydroxides*, Springer, 2006.
9. V. Rives, *Layered Double Hydroxides: Present and Future*, Nova Science Publishers, 2001.
10. R. Ma, Z. Liu, L. Li, N. Iyi and T. Sasaki, *J. Mater. Chem.*, 2006, **16**, 3809-3813.
11. Q. Wang, H. H. Tay, Z. Guo, L. Chen, Y. Liu, J. Chang, Z. Zhong, J. Luo and A. Borgna, *Appl. Clay Sci.*, 2012, **55**, 18-26.
12. T. Hibino and W. Jones, *J. Mater. Chem.*, 2001, **11**, 1321-1323.
13. Q. Wang and D. O'Hare, *Chem. Rev.*, 2012, **112**, 4124-4155.
14. S. O'Leary, D. O'Hare and G. Seeley, *Chem. Commun.*, 2002, 1506-1507.
15. M. Adachi Pagano, C. Forano and J. P. Besse, *Chem. Commun.*, 2000, 91-92.
16. Q. Wu, A. Olafsen, Ø. B. Vistad, J. Roots and P. Norby, *J. Mater. Chem.*, 2005, **15**, 4695-4700.
17. Q. Wang and D. O'Hare, *Chem. Commun.*, 2013, **49**, 6301-6303.
18. M. Yang, O. McDermott, J. C. Buffet and D. O'Hare, *RSC Adv.*, 2014, **4**, 51676-51682.
19. C. Chen, M. Yang, Q. Wang, J. C. Buffet and D. O'Hare, *J. Mater. Chem. A*, 2014, **2**, 15102-15110.
20. C. Chen, A. Wangriya, J. C. Buffet and D. O'Hare, *Dalton Trans.*, 2015, **44**, 16392-16398.
21. V. Erastova, M. T. Degiacomi, D. O'Hare and H. C. Greenwell, *RSC Adv.*, 2017, **7**, 5076-5083.
22 L. Pauling, The Nature of the Chemical Bond and the Structure of Molecules and Crystals: An Introduction to Modern Structural Chemistry, Cornell University Press, 1960.
23. A. D. McNaught and A. Wilkinson, *IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book")*, WileyBlackwell; 2nd Revised edition edition.
24. G. R. Desiraju and T. Steiner, *The weak hydrogen bond: in structural chemistry and biology*, Oxford University Press, 2001.
25. L. C. Allen and P. A. Kollman, *Chem. Rev*, 1972, **72**, 283.
26. E. S. Kryachko, A. Karpfen and F. Remacle, *J. Phys. Chem. A*, 2005, **109**, 7309-7318.

